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(54) Title: MOLECULAR SIEVE COMPOSITIONS, CATALYST THEREOF, THEIR MAKING AND USE IN CONVERSION PROCESSES

(57) Abstract: The invention relates to a catalyst composition, a method of making the same and its use in the conversion of a feedstock, preferably an oxygenated feedstock, into one or more olefins, preferably ethylene and/or propylene. The catalyst composition comprises a molecular sieve and at least one metal oxide, such as magnesium oxide that, when saturated with acetone and contacted with said acetone for 1 hour at 25 °C, converts more than 80 % of the acetone.

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MOLECULAR SIEVE COMPOSITIONS, CATALYST THEREOF,
THEIR MAKING AND USE IN CONVERSION PROCESSES

[0001] The present invention relates to molecular sieve compositions and catalysts containing the same, to the synthesis of such compositions and catalysts and to the use of such compositions and catalysts in conversion processes to produce olefin(s).

[0002] Olefins are traditionally produced from petroleum feedstocks by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s), such as ethylene and/or propylene, from a variety of hydrocarbon feedstocks. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds.

[0003] The petrochemical industry has known for some time that oxygenates, especially alcohols, are convertible into light olefin(s). The preferred alcohol for light olefin production is methanol and the preferred process for converting a methanol-containing feedstock into light olefin(s), primarily ethylene and/or propylene, involves contacting the feedstock with a molecular sieve catalyst composition.

[0004] There are many different types of molecular sieve known to convert oxygenate containing feedstocks into one or more olefin(s). For example, U.S. Patent No. 5,367,100 describes the use of the zeolite, ZSM-5, to convert methanol into olefin(s); U.S. Patent No. 4,062,905 discusses the conversion of methanol and other oxygenates to ethylene and propylene using crystalline aluminosilicate zeolites, for example Zeolite T, ZK5, erionite and chabazite; U.S. Patent No. 4,079,095 describes the use of ZSM-34 to convert methanol to hydrocarbon products such as ethylene and propylene; and U.S. Patent No. 4,310,440 describes producing light olefin(s) from an alcohol using a crystalline aluminophosphate, often designated AlPO_4 .

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[0005] Some of the most useful molecular sieves for converting methanol to olefin(s) are silicoaluminophosphate (SAPO) molecular sieves.

Silicoaluminophosphate molecular sieves contain a three-dimensional microporous crystalline framework structure of $[\text{SiO}_2]$, $[\text{AlO}_2]$ and $[\text{PO}_2]$ corner sharing tetrahedral units. Synthesis of a SAPO molecular sieve, its formulation into a catalyst, and its use in converting a feedstock into olefin(s), particularly where the feedstock is methanol, are disclosed in U.S. Patent Nos. 4,499,327, 4,677,242, 4,677,243, 4,873,390, 5,095,163, 5,714,662 and 6,166,282, all of which are herein fully incorporated by reference.

[0006] When used in the conversion of methanol to olefins, most molecular sieves, including SAPO molecular sieves, undergo rapid coking and hence require frequent regeneration, typically involving exposure of the catalyst to high temperatures and steaming environments. As a result, current methanol conversion catalysts tend to have a limited useful lifetime and hence there is a need to provide a molecular sieve catalyst composition which exhibits an enhanced lifetime particularly when used in the conversion of methanol to olefins.

[0007] U.S. Patent No. 4,465,889 describes a catalyst composition comprising a silicalite molecular sieve impregnated with a thorium, zirconium, or a titanium metal oxide for use in converting methanol, dimethyl ether, or a mixture thereof into a hydrocarbon product rich in iso- C_4 compounds.

[0008] U.S. Patent No. 6,180,828 discusses the use of a modified molecular sieve to produce methylamines from methanol and ammonia, where for example, a silicoaluminophosphate molecular sieve is combined with one or more modifiers, such as a zirconium oxide, a titanium oxide, a yttrium oxide, montmorillonite or kaolinite.

[0009] U.S. Patent No. 5,417,949 relates to a process for converting noxious nitrogen oxides in an oxygen containing effluent into nitrogen and water using a molecular sieve and a metal oxide binder, where the preferred binder is titania and the molecular sieve is an aluminosilicate.

[0010] EP-A-312981 discloses a process for cracking vanadium-containing hydrocarbon feed streams using a catalyst composition comprising a physical mixture of a zeolite embedded in an inorganic refractory matrix material and at least one oxide of beryllium, magnesium, calcium, strontium, barium or lanthanum, preferably magnesium oxide, on a silica-containing support material.

[0011] Kang and Inui, *Effects of decrease in number of acid sites located on the external surface of Ni-SAPO-34 crystalline catalyst by the mechanochemical method*, Catalysis Letters 53, pages 171-176 (1998) disclose that the shape selectivity can be enhanced and the coke formation mitigated in the conversion of methanol to ethylene over Ni-SAPO-34 by milling the catalyst with MgO, CaO, BaO or Cs₂O on microspherical non-porous silica, with BaO being most preferred.

[0012] International Publication No. WO 98/29370 discloses the conversion of oxygenates to olefins over a small pore non-zeolitic molecular sieve containing a metal selected from the group consisting of a lanthanide, an actinide, scandium, yttrium, a Group 4 metal, a Group 5 metal or combinations thereof.

[0013] In one aspect, the invention resides in a catalyst composition comprising:

- (a) a metal oxide which has a surface area greater than 20 m²/g, which has been calcined at temperature greater than 200°C, and which, when saturated with acetone and contacted with said acetone for 1 hour at 25°C, converts more than 80% of the acetone;
- (b) a binder;
- (c) a matrix material; and
- (d) a molecular sieve having an average pore size less than 5Å.

[0014] The molecular sieve conveniently comprises a framework including at least [AlO₄] and [PO₄] tetrahedral units and more particularly a framework including at least [SiO₄], [AlO₄] and [PO₄] tetrahedral units, such as a silicoaluminophosphate.

[0015] In one embodiment, the metal oxide includes magnesium oxide.

[0016] In another aspect, the invention resides in a catalyst composition comprising a molecular sieve and at least one oxide of a metal selected from Group 2 of the Periodic Table of Elements, wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m² of the metal oxide.

[0017] Conveniently, the catalyst composition also comprises at least one oxide of a metal selected from Group 3 of the Periodic Table of Elements, such as yttrium oxide, lanthanum oxide, scandium oxide and mixtures thereof.

[0018] In another aspect, the invention resides in a method for making a catalyst composition, the method comprising physically mixing first particles comprising a molecular sieve with second particles comprising at least one oxide of a metal selected from Group 2 of the Periodic Table of Elements, wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m² of the metal oxide.

[0019] In another aspect, the invention resides in a method for making a catalyst composition, the method comprising combining a silicoaluminophosphate molecular sieve, a binder, a matrix material, and at least one metal oxide that, when saturated with acetone and contacted with said acetone for 1 hour at 25°C, converts more than 25 % of the acetone.

[0020] In yet another aspect, the invention resides in a method of making a catalyst composition, the method comprising (a) combining a molecular sieve, a binder and a matrix material to produce a catalyst precursor; and (b) adding to the catalyst precursor a metal oxide that has been calcined to a temperature in the range of from 200°C to 700°C.

[0021] In one embodiment, the metal oxide is magnesium oxide and is physically mixed with a molecular sieve synthesized from a reaction mixture comprising at least one templating agent and at least two of a silicon source, a phosphorous source and an aluminum source.

[0022] In a further aspect, the invention resides in a process for converting a feedstock into one or more olefin(s) in the presence of a molecular sieve catalyst

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composition comprising a molecular sieve, a binder, a matrix material and an active metal oxide that, when saturated with acetone and contacted with said acetone for 1 hour at 25°C, converts more than 80% of the acetone.

[0023] In yet a further aspect, the invention resides in a process for producing one or more olefin(s), the process comprising contacting a feedstock comprising at least one oxygenate with a catalyst composition comprising a small pore molecular sieve, a binder, a matrix material, a magnesium oxide that has been calcined in the temperature range of from 200°C to 600°C, and a Group 3 metal oxide.

[0024] The invention relates to a catalyst composition, its synthesis and its use in the conversion of hydrocarbon feedstocks, particularly oxygenated feedstocks, into olefin(s). It has been found that combining a molecular sieve with a particular metal oxide results in a catalyst composition with a longer catalyst lifetime when used in the conversion of feedstocks, such as oxygenates, more particularly methanol, into olefin(s). In addition, the resultant catalyst composition tends to be more propylene selective and to yield lower amounts of unwanted ethane and propane. The preferred metal oxide is an oxide of a Group 2 metal having an uptake of carbon dioxide at 100°C of at least 0.03 mg/m² of the metal oxide and/or a metal oxide that is capable of converting greater than 80% of acetone at room temperature. In one embodiment, the metal oxide is magnesium oxide which has a surface area greater than 20 m²/g and which has been calcined at temperature greater than 200°C. This unexpected result is further enhanced when an oxide of a Group 3 metal (for example scandium, lanthanum, or yttrium) from the Periodic Table of Elements using the IUPAC format described in the *CRC Handbook of Chemistry and Physics*, 78th Edition, CRC Press, Boca Raton, Florida (1997) is combined with the magnesium oxide.

Molecular Sieves

[0025] Molecular sieves have been classified by the Structure Commission of the International Zeolite Association according to the rules of the IUPAC Commission on Zeolite Nomenclature. According to this classification, framework-type zeolite and zeolite-type molecular sieves, for which a structure has been established, are assigned a three letter code and are described in the *Atlas of Zeolite Framework Types*, 5th edition, Elsevier, London, England (2001), which is herein fully incorporated by reference.

[0026] Non-limiting examples of preferred molecular sieves, particularly for use in converting an oxygenate containing feedstock into olefin(s), include framework types AEL, AFY, AEI, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TAM and TON. In one preferred embodiment, the molecular sieve employed in the catalyst composition of the invention has an AEI topology or a CHA topology, or a combination thereof, most preferably a CHA topology.

[0027] Crystalline molecular sieve materials have a 3-dimensional, four-connected framework structure of corner-sharing $[TO_4]$ tetrahedra, where T is any tetrahedrally coordinated cation, such as $[SiO_4]$, $[AlO_4]$ and/or $[PO_4]$ tetrahedral units. The molecular sieves useful herein conveniently comprise a framework including $[AlO_4]$ and $[PO_4]$ tetrahedral units, i.e., an aluminophosphate (AIPO) molecular sieve, or $[SiO_4]$, $[AlO_4]$ and $[PO_4]$ tetrahedral units, i.e., a silicoaluminophosphate (SAPO) molecular sieve. Most preferably, the molecular sieves useful herein is a silicoaluminophosphate (SAPO) molecular sieve or a substituted, preferably a metal substituted, SAPO molecular sieve. Examples of suitable metal substituents are an alkali metal of Group 1 of the Periodic Table of Elements, an alkaline earth metal of Group 2 of the Periodic Table of Elements, a rare earth metal of Group 3 of the Periodic Table of Elements, including the Lanthanides: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium, dysprosium, holmium, erbium, thulium, ytterbium

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and lutetium; and scandium or yttrium, a transition metal of Groups 4 to 12 of the Periodic Table of Elements, or mixtures of any of these metal species.

[0028] Preferably, the molecular sieve used herein has a pore system defined by an 8-membered ring of $[TO_4]$ tetrahedra and has an average pore size less than 5\AA , such as in the range of from 3\AA to 5\AA , for example from 3\AA to 4.5\AA , and particularly from 3.5\AA to 4.2\AA .

[0029] Non-limiting examples of SAPO and AlPO molecular sieves useful herein include one or a combination of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44 (U.S. Patent No. 6,162,415), SAPO-47, SAPO-56, AlPO-5, AlPO-11, AlPO-18, AlPO-31, AlPO-34, AlPO-36, AlPO-37, AlPO-46, and metal containing molecular sieves thereof. Of these, particularly useful molecular sieves are one or a combination of SAPO-18, SAPO-34, SAPO-35, SAPO-44, SAPO-56, AlPO-18 and AlPO-34 and metal containing derivatives thereof, such as one or a combination of SAPO-18, SAPO-34, AlPO-34 and AlPO-18, and metal containing derivatives thereof, and especially one or a combination of SAPO-34 and AlPO-18, and metal containing derivatives thereof.

[0030] In an embodiment, the molecular sieve is an intergrowth material having two or more distinct crystalline phases within one molecular sieve composition. In particular, intergrowth molecular sieves are described in the U.S. Patent Application Publication No. 2002-0165089 and International Publication No. WO 98/15496 published April 16, 1998, both of which are herein fully incorporated by reference. For example, SAPO-18, AlPO-18 and RUW-18 have an AEI framework-type, and SAPO-34 has a CHA framework-type. Thus the molecular sieve used herein may comprise at least one intergrowth phase of AEI and CHA framework-types, especially where the ratio of CHA framework-type to AEI framework-type, as determined by the DIFFaX method disclosed in U.S. Patent Application Publication No. 2002-0165089, is greater than 1:1.

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[0031] Preferably, where the molecular sieve is a silicoaluminophosphate, the molecular sieve has a Si/Al ratio less than or equal to 0.65, such as from 0.65 to 0.10, preferably from 0.40 to 0.10, more preferably from 0.32 to 0.10, and most preferably from 0.32 to 0.15.

[0032] In one particular embodiment, the molecular sieve is SAPO-18, SAPO-34, or an intergrowth thereof in which the framework of the molecular sieves consists essentially of $[\text{SiO}_4]$, $[\text{AlO}_4]$ and $[\text{PO}_4]$ tetrahedral units and hence is free of additional framework elements, such as nickel.

Metal Oxides

[0033] The metal oxides of the invention are those metal oxides, different from typical binders and/or matrix materials, that, when used in combination with a molecular sieve, provide benefits in catalytic conversion processes. In particular, the metal oxides useful herein are oxides that, when saturated with acetone and allowed to stand in contact with the acetone for 1 hour at room temperature (about 25°C), convert greater than 80% of the acetone, for example greater than 85%, such as greater than 90%, and in some cases greater than 95%. There are a variety of methods for determining the conversion of acetone, and one such method is the use of ^{13}C solid state NMR. In this method, the metal oxide is first dehydrated under vacuum while being heated by the use of a stepwise temperature program. Typically, the highest temperature used in the dehydration procedure is 400°C. The metal oxide is then saturated with acetone-2- ^{13}C at room temperature (ca. 25°C) by the use of conventional vacuum line technique. The metal oxide with adsorbed acetone-2- ^{13}C is transferred into a 7-mm NMR rotor without any contact with air or moisture. Quantitative ^{13}C solid state NMR spectra with Magic Angle Spinning are acquired to determine the conversion of acetone after the sample has been kept at 25°C for 1 hour.

[0034] Suitable metal oxides are oxides of Group 2 metals, either alone or in combination with Group 3 metal oxides, which have an uptake of carbon dioxide

at 100°C of at least 0.03 mg/m² of the metal oxide, such as at least 0.35mg/m² of the metal oxide. Although the upper limit on the carbon dioxide uptake of the metal oxide is not critical, in general the metal oxides useful herein will have a carbon dioxide at 100°C of less than 10 mg/m² of the metal oxide, such as less than 5 mg/m² of the metal oxide.

[0035] In order to determine the carbon dioxide uptake of a metal oxide, the following procedure is adopted using a Mettler TGA/SDTA 851 thermogravimetric analysis system under ambient pressure. A sample of the metal oxide is sample is dehydrated in flowing air to about 500°C for one hour. The temperature of the sample is then reduced in flowing helium to 100°C. After the sample has equilibrated at the desired adsorption temperature in flowing helium, the sample is subjected to 20 separate pulses (about 12 seconds/pulse) of a gaseous mixture comprising 10-weight % carbon dioxide with the remainder being helium. After each pulse of the adsorbing gas the metal oxide sample is flushed with flowing helium for 3 minutes. The increase in weight of the sample in terms of mg/mg adsorbent based on the adsorbent weight after treatment at 500°C is the amount of adsorbed carbon dioxide. The surface area of the sample is measured in accordance with the method of Brunauer, Emmett, and Teller (BET) published as ASTM D 3663 to provide the carbon dioxide uptake in terms of mg carbon dioxide/m² of the metal oxide.

[0036] The most preferred Group 2 metal oxide is a magnesium oxide (MgO). Suitable Group 3 metal oxides include yttrium oxide, lanthanum oxide, scandium oxide and mixtures thereof.

[0037] In one embodiment, the active metal oxide, preferably the MgO, even more preferably the combination of the MgO and a Group 3 metal oxide, has a surface area as measured in accordance with the method of Brunauer, Emmett, and Teller (BET) published as ASTM D 3663 of greater than 20 m²/g, such as greater than 50 m²/g, for example greater than 80 m²/g, and even greater than 200 m²/g. Suitable metal oxides are those metal oxides that have a surface area greater

than 20 m²/g, that have been calcined to greater than 200°C, and are capable of converting greater than 25%, such as greater than 50%, for example greater than 80% of acetone at room temperature.

[0038] In another embodiment, the metal oxide, preferably the magnesium oxide, even more preferably the MgO and a Group 3 metal oxide, is calcined at a temperature in the range of from 200 °C to 700°C, such as from about 250°C to 650°C, for example in the range of from 300°C to 600°C, and typically from 350°C to 550°C.

[0039] In one embodiment, the magnesium metal oxide has a surface area of about 250 m²/g, and/or the magnesium oxide is calcined to about 550 °C.

[0040] The active metal oxides can be prepared using a variety of methods. The active metal oxides can be made from active metal oxide precursors, such as metal salts, preferably Group 2 or Group 3 metal salt precursors. Other suitable sources of the Group 2 metal oxide include compounds that form these metal oxides during calcination, such as oxychlorides and nitrates. A further suitable source of the Group 2 or Group 3 metal oxides include salts containing the cation of the Group 2 or Group 3 metals, such as halides, nitrates, and acetates. Alkoxides are also sources of the Group 2 or Group 3 metal oxides.

[0041] In one method, the active metal oxide is prepared by the thermal decomposition of metal-containing compounds, such as magnesium oxalate and barium oxalate, at high temperatures, such as 600°C, in flowing air. Thus prepared metal oxides usually have low BET surface area, e.g., less than 30 m²/g.

[0042] In another method, the active metal oxide is prepared by the hydrolysis of metal-containing compounds followed by dehydration and calcination. For example, MgO is hydroxylated by mixing the oxide with deionized water, forming a white slurry. The slurry is slowly heated to dryness on a heating plate to form white powder. The white powder is further dried in a vacuum oven at 100°C for at least 4 hrs, such as for 12 hrs. The dried white powder is then calcined in air at a temperature of at least 400°C, such as at least

500°C, and typically at least 550°C. Thus-prepared active metal oxides generally have higher BET surface area (between 30 to 300 m²/g) than that prepared by thermal decomposition of the active metal oxide precursors.

[0043] In yet another method, the active metal oxide is prepared by the so-called aerogel method (Koper, O. B., Lagadic, I., Volodin, A. and Klabunde, K. J. *Chem. Mater.* 1997, 9, 2468-2480). In this method, Mg powder is reacted under nitrogen purge with anhydrous methanol to form Mg(OCH₃)₂ solution in methanol. The resultant Mg(OCH₃)₂ solution is added to toluene. Water is then added dropwise to the Mg(OH)₂ solution in methanol-toluene under vigorous stirring. The resultant colloidal suspension of Mg(OH)₂ is placed in an autoclave, pressurized to 100 psig (690 kPag) with dry nitrogen, and heated slowly to a final pressure of about 1000 psig (6895 kPag). The supercritical solvent is vented to produce a fine white powder of Mg(OH)₂. Nanocrystalline MgO is obtained by heating the fine white powder at 400 °C under vacuum. Such prepared active metal oxides have the highest BET surface area, generally greater than 300 m²/g.

[0044] Various methods exist for making mixed metal oxides from Group 2 and Group 3 metal oxide precursors, e.g., wet impregnation, incipient wetness and co-precipitation.

[0045] In one embodiment, mixed metal oxides are prepared by impregnating a Group 3 metal oxide precursor onto a Group 2 metal oxide. In a typical preparation, a Group 3 metal oxide precursor such as La(acetylacetonate)₃ is dissolved in an organic solvent such as toluene. The amount of solvent used is enough to fill the mesoporous and macroporous volume of the Group 2 metal oxide. The Group 3 metal oxide precursor solution is added dropwise to the Group 2 metal oxide. The wet mixture is dried in a vacuum oven for 1 to 12 hours to remove the solvent. The resulting solid mixture is then calcined at a temperature, e.g., 400°C, high enough to decompose the Group 3 metal oxide precursor into an oxide.

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[0046] In another embodiment, a mixed oxide is prepared by the incipient wetness technique. Typically, a Group 3 metal oxide precursor such as lanthanum acetate is dissolved in deionized water. The solution is added dropwise to a Group 2 metal oxide. The mixture is dried in a vacuum oven at 50°C for 1 to 12 hours. The dried mixture is broken up and calcined at 550 °C in air for 3 hours.

[0047] In yet another embodiment, a mixed metal oxide is prepared by co-precipitation. An aqueous solution comprising Group 2 and Group 3 metal oxide precursors is subject to conditions sufficient to cause precipitation of a hydrated precursor of the solid oxide materials, such as by the addition of sodium hydroxide or ammonium hydroxide. The temperature at which the liquid medium is maintained during the co-precipitation is typically from 20°C to 100°C. The resulting gel is then hydrothermally treated at temperatures between 50 and 100 °C for several days. The hydrothermal treatment typically takes place at greater than atmospheric pressure.

[0048] The resulting material is then recovered, for example by filtration or centrifugation, and washed and dried. The resulting material is then calcined at a temperature of greater than 200°C, preferably greater than 300°C, and more preferably greater 400°C, and most preferably greater than 450°C.

Molecular Sieve Composition

[0049] The catalyst composition of the invention includes any one of the molecular sieves previously described and one or more active metal oxides described above, optionally together with a binder and/or matrix material different from the active metal oxide(s). Typically, the weight ratio of the active metal oxide(s) to the molecular sieve in the catalyst composition is in the range of from 1 weight percent to 800 weight percent, such as from 5 weight percent to 200 weight percent, particularly from 10 weight percent to 100 weight percent.

[0050] There are many different binders that are useful in forming catalyst compositions. Non-limiting examples of binders that are useful alone or in

combination include various types of hydrated alumina, silicas, and/or other inorganic oxide sols. One preferred alumina containing sol is aluminum chlorhydrol. The inorganic oxide sol acts like glue binding the synthesized molecular sieves and other materials such as the matrix together, particularly after thermal treatment. Upon heating, the inorganic oxide sol, preferably having a low viscosity, is converted into an inorganic oxide binder component. For example, an alumina sol will convert to an aluminum oxide binder following heat treatment.

[0051] Aluminum chlorhydrol, a hydroxylated aluminum based sol containing a chloride counter ion, has the general formula of $Al_mO_n(OH)_oCl_p \cdot x(H_2O)$ wherein m is 1 to 20, n is 1 to 8, o is 5 to 40, p is 2 to 15, and x is 0 to 30. In one embodiment, the binder is $Al_{13}O_4(OH)_{24}Cl_7 \cdot 12(H_2O)$ as is described in G.M. Wolterman, et al., Stud. Surf. Sci. and Catal., 76, pages 105-144 (1993), which is herein incorporated by reference. In another embodiment, one or more binders are combined with one or more other non-limiting examples of alumina materials such as aluminum oxyhydroxide, γ -alumina, boehmite, diaspora, and transitional aluminas such as α -alumina, β -alumina, γ -alumina, δ -alumina, ϵ -alumina, κ -alumina, and ρ -alumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyleite, and mixtures thereof.

[0052] In another embodiment, the binder is an alumina sol, predominantly comprising aluminum oxide, optionally including some silicon. In yet another embodiment, the binder is peptized alumina made by treating an alumina hydrate, such as pseudoboehmite, with an acid, preferably an acid that does not contain a halogen, to prepare a sol or aluminum ion solution. Non-limiting examples of commercially available colloidal alumina sols include Nalco 8676 available from Nalco Chemical Co., Naperville, Illinois, and Nyacol AL20DW available from Nyacol Nano Technologies, Inc., Ashland, Massachusetts.

[0053] Where the catalyst composition contains a matrix material, this is preferably different from the active metal oxide and any binder. Matrix materials are typically effective in reducing overall catalyst cost, acting as thermal sinks to

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assist in shielding heat from the catalyst composition for example during regeneration, densifying the catalyst composition, and increasing catalyst strength such as crush strength and attrition resistance.

[0054] Non-limiting examples of matrix materials include one or more non-active metal oxides including beryllia, quartz, silica or sols, and mixtures thereof, for example silica-magnesia, silica-zirconia, silica-titania, silica-alumina and silica-alumina-thoria. In an embodiment, matrix materials are natural clays such as those from the families of montmorillonite and kaolin. These natural clays include subbentonites and those kaolins known as, for example, Dixie, McNamee, Georgia and Florida clays. Non-limiting examples of other matrix materials include halosite, kaolinite, dickite, nacrite, or anauxite. The matrix material, such as a clay, may be subjected to well known modification processes such as calcination and/or acid treatment and/or chemical treatment.

[0055] In a preferred embodiment, the matrix material is a clay or a clay-type composition, particularly a clay or clay-type composition having a low iron or titania content, and most preferably the matrix material is kaolin. Kaolin has been found to form a pumpable, high solids content slurry, to have a low fresh surface area, and to pack together easily due to its platelet structure. A preferred average particle size of the matrix material, most preferably kaolin, is from about 0.1 μm to about 0.6 μm with a D_{90} particle size distribution of less than about 1 μm .

[0056] Where the catalyst composition contains a binder or matrix material, the catalyst composition typically contains from 1% to 80%, such as from 5% to 60%, and particularly from 5% to 50%, by weight of the molecular sieve based on the total weight of the catalyst composition.

[0057] Where the catalyst composition contains a binder and a matrix material, the weight ratio of the binder to the matrix material is typically from 1:15 to 1:5, such as from 1:10 to 1:4, and particularly from 1:6 to 1:5. The amount of binder is typically from 2% by weight to 30% by weight, such as from

5% by weight to 20% by weight, and particularly from 7% by weight to 15% by weight, based on the total weight of the binder, the molecular sieve and matrix material. It has been found that a higher sieve content and lower matrix content increases the molecular sieve catalyst composition performance, whereas a lower sieve content and higher matrix content improves the attrition resistance of the composition.

[0058] The catalyst composition typically has a density in the range of from 0.5 g/cc to 5 g/cc, such as from 0.6 g/cc to 5 g/cc, for example from 0.7 g/cc to 4 g/cc, particularly in the range of from 0.8 g/cc to 3 g/cc.

Method of Making The Catalyst Composition

[0059] In making the catalyst composition, the molecular sieve is first formed and is then physically mixed with the Group 2 metal oxide described above, or with a mixture of Group 2 and Group 3 metal oxides, preferably in a substantially dry, dried, or calcined state. Most preferably the molecular sieve and active metal oxides are physically mixed in their calcined state. Without being bound by any particular theory, it is believed that intimate mixing of the molecular sieve and one or more active metal oxides improves conversion processes using the molecular sieve composition and catalyst composition of the invention. Intimate mixing can be achieved by any method known in the art, such as mixing with a mixer muller, drum mixer, ribbon/paddle blender, kneader, or the like. Chemical reaction between the molecular sieve and the metal oxide(s) is unnecessary and, in general, is not preferred.

[0060] Where the catalyst composition contains a matrix and/or binder, the molecular sieve is conveniently initially formulated into a catalyst precursor with the matrix and/or binder and the active metal oxide is then combined with the formulated precursor. The active metal oxide can be added as unsupported particles or can be added in combination with a support, such as a binder or matrix material. The resultant catalyst composition can then be formed into useful

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shaped and sized particles by well-known techniques such as spray drying, pelletizing, extrusion, and the like.

[0061] In one embodiment, the molecular sieve composition and the matrix material, optionally with a binder, are combined with a liquid to form a slurry and then mixed to produce a substantially homogeneous mixture containing the molecular sieve composition. Non-limiting examples of suitable liquids include water, alcohol, ketones, aldehydes, and/or esters. The most preferred liquid is water. The slurry of the molecular sieve composition, binder and matrix material is then fed to a forming unit, such as spray drier, that forms the catalyst composition into the required shape, for example microspheres.

[0062] Once the molecular sieve catalyst composition is formed in a substantially dry or dried state, to further harden and/or activate the formed catalyst composition, a heat treatment such as calcination, at an elevated temperature is usually performed. Typical calcination temperatures are in the range from 400°C to 1,000°C, such as from 500°C to 800°C, for example from 550°C to 700°C. Typical calcination environments are air (which may include a small amount of water vapor), nitrogen, helium, flue gas (combustion product lean in oxygen), or any combination thereof.

[0063] In a preferred embodiment, the catalyst composition is heated in nitrogen at a temperature of from 600°C to 700°C. Heating is carried out for a period of time typically from 30 minutes to 15 hours, such as from 1 hour to 10 hours, for example from 1 hour to 5 hours, and particularly from 2 hours to 4 hours.

Process For Using the Molecular Sieve Catalyst Compositions

[0064] The catalyst compositions described above are useful in a variety of processes including cracking, of for example a naphtha feed to light olefin(s) (U.S. Patent No. 6,300,537) or higher molecular weight (MW) hydrocarbons to lower MW hydrocarbons; hydrocracking, of for example heavy petroleum and/or cyclic

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feedstock; isomerization, of for example aromatics such as xylene; polymerization, of for example one or more olefin(s) to produce a polymer product; reforming; hydrogenation; dehydrogenation; dewaxing, of for example hydrocarbons to remove straight chain paraffins; absorption, of for example alkyl aromatic compounds for separating out isomers thereof; alkylation, of for example aromatic hydrocarbons such as benzene and alkyl benzene, optionally with propylene to produce cumene or with long chain olefins; transalkylation, of for example a combination of aromatic and polyalkylaromatic hydrocarbons; dealkylation; hydrodeacylation; disproportionation, of for example toluene to make benzene and paraxylene; oligomerization, of for example straight and branched chain olefin(s); and dehydrocyclization.

[0065] Preferred processes include processes for converting naphtha to highly aromatic mixtures; converting light olefin(s) to gasoline, distillates and lubricants; converting oxygenates to olefin(s); converting light paraffins to olefins and/or aromatics; and converting unsaturated hydrocarbons (ethylene and/or acetylene) to aldehydes for conversion into alcohols, acids and esters.

[0066] The most preferred process of the invention is the conversion of a feedstock to one or more olefin(s). Typically, the feedstock contains one or more aliphatic-containing compounds, and preferably one or more oxygenates, such that the aliphatic moiety contains from 1 to about 50 carbon atoms, preferably from 1 to 20 carbon atoms, more preferably from 1 to 10 carbon atoms, and most preferably from 1 to 4 carbon atoms.

[0067] Non-limiting examples of suitable aliphatic-containing compounds include alcohols such as methanol and ethanol, alkyl mercaptans such as methyl mercaptan and ethyl mercaptan, alkyl sulfides such as methyl sulfide, alkylamines such as methylamine, alkyl ethers such as dimethyl ether, diethyl ether and methylethyl ether, alkyl halides such as methyl chloride and ethyl chloride, alkyl ketones such as dimethyl ketone, formaldehydes, and various acids such as acetic acid. Preferably, the feedstock comprises methanol, ethanol, dimethyl ether,

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diethyl ether or a combination thereof, more preferably methanol and/or dimethyl ether, and most preferably methanol.

[0068] Using the various feedstocks discussed above, particularly a feedstock containing an oxygenate, such as an alcohol, the catalyst composition of the invention is effective to convert the feedstock primarily into one or more olefin(s). The olefin(s) produced typically have from 2 to 30 carbon atoms, preferably 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbons atoms, and most preferably are ethylene and/or propylene.

[0069] Typically, the catalyst composition of the invention is effective to convert a feedstock containing one or more oxygenates into a product containing greater than 50 weight percent, typically greater than 60 weight percent, such as greater than 70 weight percent, and preferably greater than 80 weight percent of olefin(s) based on the total weight of hydrocarbon in the product. Moreover, the amount of ethylene and/or propylene produced based on the total weight of hydrocarbon in the product is typically greater than 40 weight percent, for example greater than 50 weight percent, preferably greater than 65 weight percent, and more preferably greater than 78 weight percent. Typically, the amount ethylene produced in weight percent based on the total weight of hydrocarbon product produced, is greater than 20 weight percent, such as greater than 30 weight percent, for example greater than 40 weight percent. In addition, the amount of propylene produced in weight percent based on the total weight of hydrocarbon product produced is greater than 20 weight percent, such as greater than 25 weight percent, for example greater than 30 weight percent, and preferably greater than 35 weight percent.

[0070] Using the catalyst composition of the invention for the conversion of a feedstock comprising methanol and dimethylether to ethylene and propylene, it is found that the production of ethane and propane is reduced by greater than 10%, such as greater than 20%, for example greater than 30%, and particularly in the

range of from 30% to 40% compared to a similar catalyst composition at the same conversion conditions but without the active metal oxide component(s).

[0071] In addition to the oxygenate component, such as methanol, the feedstock may contain one or more diluents, which are generally non-reactive to the feedstock or molecular sieve catalyst composition and are typically used to reduce the concentration of the feedstock. Non-limiting examples of diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water, essentially non-reactive paraffins (especially alkanes such as methane, ethane, and propane), essentially non-reactive aromatic compounds, and mixtures thereof. The most preferred diluents are water and nitrogen, with water being particularly preferred.

[0072] The present process can be conducted over a wide range of temperatures, such as in the range of from 200°C to 1000°C, for example from 250°C to 800°C, including from 250°C to 750 °C, conveniently from 300°C to 650°C, preferably from 350°C to 600°C and more preferably from 350°C to 550°C.

[0073] Similarly, the present process can be conducted over a wide range of pressures including autogenous pressure. Typically the partial pressure of the feedstock exclusive of any diluent therein employed in the process is in the range of from 0.1 kPaa to 5 MPaa, preferably from 5 kPaa to 1 MPaa, and more preferably from 20 kPaa to 500 kPaa.

[0074] The weight hourly space velocity (WHSV), defined as the total weight of feedstock excluding any diluents per hour per weight of molecular sieve in the catalyst composition, can range from 1 hr⁻¹ to 5000 hr⁻¹, preferably from 2 hr⁻¹ to 3000 hr⁻¹, more preferably from 5 hr⁻¹ to 1500 hr⁻¹, and most preferably from 10 hr⁻¹ to 1000 hr⁻¹. In one embodiment, the WHSV is at least 20 hr⁻¹ and, where the feedstock contains methanol and/or dimethyl ether, is in the range of from 20 hr⁻¹ to 300 hr⁻¹.

[0075] The process of the invention is conveniently conducted as a fixed bed process, or more typically as a fluidized bed process (including a turbulent bed process), such as a continuous fluidized bed process, and particularly a continuous high velocity fluidized bed process.

[0076] In one practical embodiment, the process is conducted as a fluidized bed process utilizing a reactor system, a regeneration system and a recovery system. In such a process, fresh feedstock, optionally with one or more diluent(s), is fed together with the molecular sieve catalyst composition into one or more riser reactor(s) in the reactor system. The feedstock is converted in the riser reactor(s) into a gaseous effluent that enters a disengaging vessel in the reactor system along with the coked catalyst composition. The coked catalyst composition is separated from the gaseous effluent within the disengaging vessel, typically with the aid of cyclones, and is then fed to a stripping zone, typically in a lower portion of the disengaging vessel. In the stripping zone the coked catalyst composition is contacted with a gas, such steam, methane, carbon dioxide, carbon monoxide, hydrogen, and/or an inert gas such as argon, preferably steam, to recover adsorbed hydrocarbons from the coked catalyst composition that is then introduced into the regeneration system.

[0077] In the regeneration system the coked catalyst composition is contacted with a regeneration medium, preferably a gas containing oxygen, under regeneration conditions capable of burning coke from the coked catalyst composition, preferably to a level less than 0.5 weight percent based on the total weight of the coked molecular sieve catalyst composition entering the regeneration system. For example, the regeneration conditions may include temperature in the range of from 450°C to 750°C, and preferably from 550°C to 700°C.

[0078] The regenerated catalyst composition withdrawn from the regeneration system is combined with fresh molecular sieve catalyst composition

and/or re-circulated molecular sieve catalyst composition and/or feedstock and/or fresh gas or liquids, and returned to the riser reactor(s).

[0079] The gaseous effluent is withdrawn from the disengaging system and is passed through a recovery system for separating and purifying the light olefin(s), particularly ethylene and propylene, in the gaseous effluent.

[0080] In one practical embodiment, the process of the invention forms part of an integrated process for producing light olefin(s) from a hydrocarbon feedstock, particularly methane and/or ethane. The first step in the process is passing the gaseous feedstock, preferably in combination with a water stream, to a syngas production zone to produce a synthesis gas stream, typically comprising carbon dioxide, carbon monoxide and hydrogen. The synthesis gas stream is then converted to an oxygenate containing stream generally by contacting with a heterogeneous catalyst, typically a copper based catalyst, at temperature in the range of from 150°C to 450°C and a pressure in the range of from 5 MPa to 10 MPa. After purification, the oxygenate containing stream can be used as a feedstock in a process as described above for producing light olefin(s), such as ethylene and/or propylene. Non-limiting examples of this integrated process are described in EP-B-0 933 345, which is herein fully incorporated by reference.

[0081] In another more fully integrated process, optionally combined with the integrated processes described above, the olefin(s) produced are directed to one or more polymerization processes for producing various polyolefins.

[0082] In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

Example A - Preparation of a Molecular Sieve

[0083] A silicoaluminophosphate molecular sieve, SAPO-34, designated as MSA, was crystallized in the presence of tetraethyl ammonium hydroxide (R1) and dipropylamine (R2) as the organic structure directing agents or templating agents. A mixture of the following mole ratio composition:

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0.2 SiO₂ / Al₂O₃ / P₂O₅ / 0.9 R1 / 1.5 R2 / 50 H₂O.

was prepared by initially mixing an amount of Condea Pural SB with deionised water, to form a slurry. To this slurry was added an amount of phosphoric acid (85%). These additions were made with stirring to form a homogeneous mixture. To this homogeneous mixture Ludox AS40 (40% of SiO₂) was added, followed by the addition of R1 with mixing to form a homogeneous mixture. To this homogeneous mixture R2 was added. This homogeneous mixture was then crystallized with agitation in a stainless steel autoclave by heating to 170°C for 40 hours. This provided a slurry of the crystalline molecular sieve. The crystals were then separated from the mother liquor by filtration. The molecular sieve crystals were then mixed with a binder and matrix material and formed into particles by spray drying.

Example B - Conversion Process

[0084] All catalytic or conversion data presented were obtained using a microflow reactor consisting of a stainless steel reactor (1/4 inch (0.64 cm) outer diameter) located in a furnace to which vaporized methanol is fed. The methanol conversion reactions were preformed at 475°C, 25 psig (172 kPag) and 100 WHSV (with respect to the amount of SAPO-34). The typical charge of formulated SAPO 34 described in Example A was 95 mg and the reactor bed was diluted with 1 gram of quartz sand to minimize the reaction exotherm in the reactor. In particular, for the catalyst composition of the invention, the molecular sieve and metal oxide, a physical mixture of the MSA molecular sieve of Example A and the active metal oxide was used.

[0085] The effluent from the reactor was collected in a 15-sample loop Valco valve. The collected samples were analyzed by on-line gas chromatography (Hewlett Packard 6890) equipped with a flame ionization detector. The chromatographic column used was a Q-column. The response factors used are listed in the following Table 1.

Table 1

| C ₁ | C ₂ = | C ₂ ^o | C ₃ = | C ₃ ^o | CH ₃ OH | (CH ₃) ₂ O | C ₄ 's | C ₅ 's | C ₆ 's | C ₇ 's |
|----------------|------------------|-----------------------------|------------------|-----------------------------|--------------------|-----------------------------------|-------------------|-------------------|-------------------|-------------------|
| 1.103 | 1.000 | 1.070 | 1.003 | 1.052 | 3.035 | 2.639 | 0.993 | 0.999 | 1.006 | 1.000 |

[0086] The terms "C₄'s, C₅+, etc." refer to the number of carbons in the hydrocarbon. Note that the selectivity designated as "C₅+'s" consist of the sum of C₅'s, C₆'s and C₇'s. The weighed averages (selectivity) were calculated based on the following formula, $x_1*y_1 + (x_2-x_1)*(y_1 + y_2)/2 + (x_3-x_2)*(y_2 + y_3)/2 + \dots$, where x_i and y_i are yield and g methanol fed/g molecular sieve, respectively. Lifetime of catalysts (g methanol/g molecular sieve) reported is methanol that was cumulatively converted. Note that both the lifetime and WHSV were reported based on the weight of the SAPO-34 sieve. Methanol converted at less than 10 weight percent conversions was not counted in the calculations. Dimethyl ether was not counted as product, instead it was treated as unreacted methanol in calculating selectivity and conversions.

Example 1 - Control Experiment

[0087] In this Example 1, the catalyst composition consisted of a molecular sieve, designated as MSA as described in Example A. The catalyst was diluted with quartz to form the reactor bed. The results of this experiment in the reactor and conditions discussed above in Example B are shown in Table 2.

Table 2

| C ₁ | C ₂ = | C ₂ ^o | C ₃ = | C ₃ ^o | C ₄ s | C ₅ ⁺ s | C ₂₊₃ = | Lifetime g/g |
|----------------|------------------|-----------------------------|------------------|-----------------------------|------------------|-------------------------------|--------------------|--------------|
| 1.77 | 37.65 | 0.29 | 39.80 | 0.63 | 13.04 | 6.82 | 77.45 | 16.34 |

Example 2 - Preparation of MgO and Acetone Conversion Measurement

[0088] The MgO was prepared as follows. 5.0 g of MgO (98%, ACS reagent grade from Aldrich) was mixed with 150 ml of deionized water to form a white slurry. The white slurry was slowly heated to dryness on a heating plate. The dried cake was broken into pieces and was ground to a fine powder. The powder was further dried in an oven at 120°C for 12 hrs. The white powder was then calcined at 550°C in air for 3 hrs. Thus the prepared active metal oxide, MgO, has a relatively high surface area (BET area of about 250 m²/g). The MgO powders were sieved to get particles of various sizes. Particle sizes between 75 to 150 micron were used in a conversion process as described in Example B.

[0089] 0.25 g of this prepared MgO was loaded into a glass tube, and the tube was connected to a vacuum line via a 9-mm O-ring joint. The MgO was then heated to 450°C and kept at 450°C for 2 hrs under vacuum to remove water from the oxide. After cooling down to room temperature, 25°C, the MgO was saturated with acetone-2-¹³C. The MgO with adsorbed acetone-2-¹³C was then loaded into a 7-mm NMR rotor without any contact with air or moisture. The sample was allowed to stay at room temperature (about 25 °C) for 1 hour prior to NMR measurement of acetone conversion. ¹³C NMR experiments were performed on a 200 MHz solid state NMR spectrometer with Magic Angle Spinning. Cross polarization spectra were acquired using 1-s pulse delay, 2-ms contact time and 2000 scans. Quantitative single pulse spectra were acquired using 15-s pulse delay and 400 or more scans. The test was repeated and results of the ¹³C NMR revealed that, on average, after 1 hour more than 80% of acetone had been consumed.

Example 3 - Molecular Sieve and MgO

[0090] In this Example 3, the molecular sieve catalyst composition consisted of 33.6 wt% of MSA, 50.4 wt% of binder and 16 wt% MgO as described in

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Example 2 above. The catalyst composition was well mixed, and then diluted with quartz to form the reactor bed. The results of this experiment in the reactor and conditions discussed above in Example B are shown in Table 3. The data in Table 2 and Table 3 illustrate that by constituting 16 wt% of the catalyst composition loading with the MgO, the lifetime of the SAPO-34 molecular sieve has increased to 31.66 g/g molecular sieve from 16.34 g/g molecular sieve, an increase of 94%.

Table 3

| C_1 | $C_2=$ | C_2^o | $C_3=$ | C_3^o | C_4s | C_5+s | $C_{2+3}=$ | Lifetime g/g |
|-------|--------|---------|--------|---------|--------|---------|------------|--------------|
| 1.73 | 36.86 | 0.27 | 40.74 | 0.53 | 14.01 | 5.87 | 77.59 | 31.66 |

Example 4 - Mixing MgO with a Group 3 Metal Oxide (5 wt% La_2O_3)

[0091] The loading of a Group 3 metal oxide where the metal is La onto the high surface area MgO was achieved via incipient wetness. 0.2261 g of Lanthanum acetate was dissolved in ca. 1.9 ml of deionized water. The solution was added drop-wise to 2.0146 g of MgO. The mixture was dried in a vacuum oven at 50 °C for 1 hr. The dried mixture was broken up and calcined at 550 °C in air for 3 hrs. The wt% of La_2O_3 is about 5 %. The metal oxides powders were sieved to get particles of various sizes. Particle sizes between 75 to 150 micron were used in a conversion process.

Example 5 - Molecular Sieve and a Mixed Metal Oxide: La_2O_3 (5 wt%)/MgO

[0092] In this Example 5, the catalyst composition consisted of 33.6 wt% of MSA, 50.4 wt% of binder and 16 wt% of MgO containing 5 weight percent of a Group 3 metal oxide wherein the metal is La, as described in Example 4 above. The catalyst composition was well mixed, and then diluted with quartz to form the reactor bed. The results of this experiment in the reactor and conditions discussed above in Example B are shown in Table 4. The data in Table 2 and Table 4

illustrate that by constituting 16 wt% of the catalyst composition load with MgO containing 5 weight percent La_2O_3 , the lifetime of the SAPO-34 molecular sieve has increased more than 300% from 16.34 g/g sieve to 65.90 g/g sieve.

Table 4

| C_1 | $C_2=$ | C_2^o | $C_3=$ | C_3^o | C_4s | C_5+s | $C_{2+3=}$ | Lifetime g/g |
|-------|--------|---------|--------|---------|--------|---------|------------|--------------------|
| 1.59 | 34.54 | 0.23 | 42.02 | 0.50 | 14.24 | 6.87 | 76.56 | 65.90 ^a |

a. the lowest conversion measured was 30.69 wt% with a lifetime of 57.57 g methanol/g sieve at that conversion. The reported lifetime (65.90 g methanol/g sieve) was estimated by extrapolating the conversion from 30.69 wt% to 10 wt%.

Comparative Example 6 - Molecular Sieve and BaO

[0093] In this Comparative Example 6, 28.8 wt% MSA, 43.2 wt% binder and 28 wt% of barium acetate were well mixed, and then diluted with quartz to form the reactor bed. The reactor was heated to 550°C and kept at 550°C for 90 min in a stream of a mixture of 20 ml/min of oxygen and 50 ml/min of He. Barium acetate was decomposed into barium oxide under these conditions. The molecular catalyst composition consisted of 32 wt% of MSA, 48 wt% of binder and 20 wt% of BaO. The reactor temperature was then lowered to 475°C, and the catalyst composition was tested in a conversion process under the conditions of Example B above. Results of the conversion process are shown in Table 5. The data in Table 2 and Table 5 illustrate that by constituting 20 wt% of the catalyst composition load with BaO, the lifetime of the SAPO-34 molecular sieve has increased 43%.

Table 5

| C_1 | $C_2=$ | C_2^o | $C_3=$ | C_3^o | C_4s | C_5+s | $C_{2+3=}$ | Lifetime g/g |
|-------|--------|---------|--------|---------|--------|---------|------------|--------------|
| 1.74 | 37.19 | 0.27 | 40.36 | 0.55 | 13.57 | 6.32 | 77.55 | 23.36 |

CLAIMS

We claim:

1. A catalyst composition comprising:
 - (a) a metal oxide which has a surface area greater than $20 \text{ m}^2/\text{g}$, which has been calcined at temperature greater than 200°C , and which, when saturated with acetone and contacted with said acetone for 1 hour at 25°C , converts more than 80% of the acetone;
 - (b) a binder;
 - (c) a matrix material; and
 - (d) a molecular sieve having an average pore size less than 5\AA .
2. The catalyst composition of claim 1 wherein the surface area of said metal oxide is greater than $70 \text{ m}^2/\text{g}$.
3. The catalyst composition of claim 1 or claim 2 wherein said metal oxide is selected from Group 2 of the Periodic Table of Elements.
4. The catalyst composition of claim 3 further comprising a Group 3 metal oxide.
5. A catalyst composition comprising a molecular sieve and at least one oxide of a metal selected from Group 2 of the Periodic Table of Elements, wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide.

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6. The catalyst composition of claim 5 wherein said metal oxide, when saturated with acetone and contacted with said acetone for 1 hour at 25°C, converts more than 80% of the acetone.
7. The catalyst composition of claim 5 or claim 6 and also including at least one of a binder and a matrix material different from said metal oxide.
8. The catalyst composition of any preceding claim and including a binder which includes an alumina sol and a matrix material which includes a clay.
9. The catalyst composition of any one of claims 5 to 8 and further comprising a Group 3 metal oxide.
10. The catalyst composition of claim 4 or claim 9 wherein the Group 3 metal oxide is selected from yttrium oxide, lanthanum oxide, scandium oxide and mixtures thereof.
11. The catalyst composition of any preceding claim wherein said metal oxide comprises a magnesium oxide.
12. The catalyst composition of any preceding claim wherein the molecular sieve comprises a silicoaluminophosphate and/or an aluminophosphate.
13. A method of making a catalyst composition, the method comprising (a) combining a silicoaluminophosphate molecular sieve and/or an aluminophosphate molecular sieve, a binder and a matrix material to produce a catalyst precursor; and (b) adding to the catalyst precursor at least one metal oxide that has been calcined to a temperature in the range of from 200°C to 700°C.

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14. A method of making a catalyst composition, the method comprising combining a silicoaluminophosphate molecular sieve and/or an aluminophosphate molecular sieve, a binder, a matrix material, and at least one metal oxide that, when saturated with acetone and contacted with said acetone for 1 hour at 25°C, converts more than 25% of the acetone.
15. The method of claim 13 or claim 14 wherein said at least one metal oxide comprises a magnesium oxide.
16. A method for making a catalyst composition, the method comprising physically mixing first particles comprising a molecular sieve with second particles comprising at least one oxide of a metal selected from Group 2 of the Periodic Table of Elements, wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m² of the metal oxide.
17. The method of claim 16 wherein at least one said first and said second particles also include at least one of a binder and a matrix material.
18. The method of claim 16 or claim 17 wherein said first particles comprise a silicoaluminophosphate molecular sieve, a binder including an alumina sol and a matrix material including a clay.
19. The method of any one claims 15 to 18 wherein said at least one metal oxide further comprises at least one oxide of a metal selected from Group 3 of the Periodic Table of Elements.

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20. A process for converting a feedstock into one or more olefin(s) in the presence of the catalyst composition prepared by the method of any one of claims 13 to 19.
21. A process for converting a feedstock into one or more olefin(s) in the presence of a molecular sieve catalyst composition comprising a molecular sieve, a binder, a matrix material and a metal oxide that, when saturated with acetone and contacted with said acetone for 1 hour at 25°C, converts more than 80% of the acetone.
22. The process of claim 21 wherein said metal oxide has been calcined to a temperature in the range of from 200°C to 700°C.
23. The process of claim 21 or claim 22 wherein the metal oxide has a surface area of greater than 70 m²/g.
24. The process of any one of claims 21 to 23 wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m² of the metal oxide.
25. The process of any one of claims 21 to 24 wherein said metal oxide comprises a magnesium oxide.
26. The process of claim 25 wherein the catalyst composition also contains a Group 3 metal oxide.
27. A process for producing one or more olefin(s), the process comprising contacting a feedstock comprising at least one oxygenate with a catalyst composition comprising a small pore molecular sieve, a binder, a matrix

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material, a magnesium oxide that has been calcined in the temperature range of from 200°C to 700°C, and a Group 3 metal oxide.

28. The process of any one of claims 20 to 27 wherein the feedstock comprises methanol and/or dimethylether.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CATALYST COMPOSITIONS COMPRISING MOLECULAR SIEVES, THEIR PREPARATION AND USE IN CONVERSION PROCESSES

(57) Abstract: The invention relates to a catalyst composition, a method of making the same and its use in the conversion of a feedstock, preferably an oxygenated feedstock, into one or more olefin(s), preferably ethylene and/or propylene. The catalyst composition comprises a molecular sieve and at least one metal oxide, such as magnesium oxide that, when saturated with acetone and contacted with said acetone for 1 hour at 25 °C, converts more than 80 % of the acetone.



WO 03/074175 A3

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 03/03951

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J29/85 B01J23/83 B01J35/00 B01J37/00 B01J37/08
C10G3/00 C07C1/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| Y | WO 02 05952 A (BARGER PAUL T ;UOP LLC (US); KARCH JOHN A (US); MARKER TERRY L (US) 24 January 2002 (2002-01-24) | 13,20 |
| A | page 10, line 12 - line 20; claims 1-10; examples 1-6 | 27,28 |
| Y | GERHARTZ W & YAMAMOTO Y S (EDS.): "Ullmann's Encyclopedia of Industrial Chemistry, Vol. A7; Edition 5" 1986, VCH VERLAG, WEINHEIM, DE XP002252573 | 13,20 |
| A | page 128; table 2 | |
| A | WO 02 05951 A (EXXONMOBIL CHEM PATENTS INC) 24 January 2002 (2002-01-24) | 13,20, 27,28 |
| | page 10, line 30 -page 11, line 8; table 1 | |
| | --- -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

* & * document member of the same patent family

Date of the actual completion of the international search

27 August 2003

Date of mailing of the international search report

06/10/2003

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INTERNATIONAL SEARCH REPORT

Internatio: lication No

PCT/US 03/03951

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | KANG M ET AL: "EFFECTS OF DECREASE IN NUMBER OF ACID SITES LOCATED ON THE EXTERNAL SURFACE OF NI-SAPO-34 CRYSTALLINE CATALYST BY THE MECHANOCHEMICAL METHOD" CATALYSIS LETTERS, BALTZER, SCIENTIFIC PUBL, BASEL, CH, vol. 53, no. 3/4, 1 August 1998 (1998-08-01), pages 171-176, XP000776707 ISSN: 1011-372X the whole document ----- | 13,20, 27,28 |
| A | EP 0 967 011 A (MITSUBISHI GAS CHEMICAL CO) 29 December 1999 (1999-12-29) paragraph '0016!; examples 1-5 ----- | 13,20 |

INTERNATIONAL SEARCH REPORT

Intern application No.
PCT/US 03/03951

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-12, 14-19, 20 (in part), 21-26
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 13,20

Method of making a catalyst composition comprising combining SAPO or ALPO, binder, and matrix and adding a metal oxide that has been calcined at 200-700°C

2. Claims: 27,28

Process for producing olefins using a catalyst composition comprising a small pore molecular sieve, binder, matrix and MgO calcined at 200-700°C.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-12, 14-19, 20 (in part), 21-26

Present claims 1-12, 14-19, 20 (in part), 21-26 relate to catalysts defined (inter alia) by reference to the ability to convert more than 80% of the acetone, when saturated with acetone and contacted with said acetone for 1 hour at 25°C.

The use of this parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art.

In addition, this parameter seems to be a desirable behaviour which is to be achieved, without giving an indication as to which physical properties of the metal oxide give rise to this behaviour. Also for this reason the claims lack clarity (Article 6 PCT).

The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to claim 13, 20 (insofar relating to the catalyst prepared by the method of claim 13) and 27-28.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/03951

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| WO 0205952 | A | 24-01-2002 | AU 7590101 A | 30-01-2002 |
| | | | CN 1341584 A | 27-03-2002 |
| | | | WO 0205952 A2 | 24-01-2002 |
| | | | ZA 200105793 A | 08-02-2002 |
| WO 0205951 | A | 24-01-2002 | US 6448197 B1 | 10-09-2002 |
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| | | | CA 2415730 A1 | 24-01-2002 |
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